INFLUENCE OF INTER-ELECTRODE SEPERATION IN HIGH FREQUENCY TITRATION

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The inter-electrode separation (Mukherjee *et al*, 1963) influences profoundly the response in titrations performed in the high frequency field A titration of 0.001N HCl with 0.025N NaOH was studied with the help of a high frequency titrimeter working on 8 Mc/s. The electrode distance of the titration cell was gradually varied and the total change in the condenser dial reading pertaining to the end point for each titration was noted. The result was shown in figure 1 whence it is evident that the response is poor at lower electrode distances but is quite satisfactory beyond 3 5 cm. where the variation in the capacitance remains constantly maximum

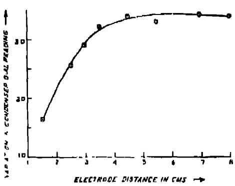


Fig. 1.

This observation can be interpreted from the properties of the circuit as follows In the present case, the titration cell is connected in parallel with other capacitors. Hence a parallel equivalent circuit is considered as the best representative of the situation whose capacitance (Delahey, 1954) is given by,

$$C_p = \frac{C_1{}^2K+\omega^2C_1C_2{}^2+\omega^2C_1{}^2C_2}{K^2+\omega^2(C_1+C_2)^2} \quad \dots \quad (1)$$

where C_p is the parallel equivalent capacitance, C_1 is the capacitance due to the dielectric properties of the walls of the container, C_2 that of the solution, K the actual low frequency conductance of the solution and $\omega = 2\pi f$, f being the frequency in cycles/sec.

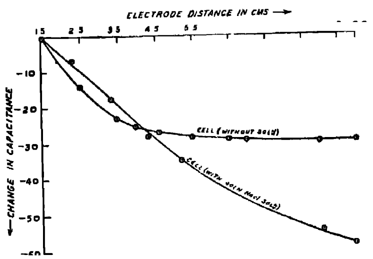
From the above equation if $K = 0$, $C_p = \frac{C_1 C_2}{C_1+C_2}$ and if $K = \infty$, the value of $C_p = C_1$. Hence the change in C (ΔC_p) represented by C in the following is given by $C = \frac{C_1^2}{C_1+C_2}$.

Here $K = 0$ represents the case of empty well without solution and the other case represents a cell filled with highly conducting electrolyte solution With the same solution and the same cell the greater the value of this C with varying electrode distance the deeper will be the titration curve (Mukherjee *et al*, 1963) If we assume this change in C to be maximum at the optimum electrode separation denoted by x, then at the point of optimum separation $\frac{dc}{dx} = 0$ whence,

$$\frac{2(C_1+C_2)}{C_1} \cdot \frac{dC_1}{dx} = \frac{d}{dx}(C_1+C_2) \tag{2}$$

Here we may regard C_1 as the capacitance when the cell is empty and (C_1+C_2) the capacitance when the cell contains the solution.

In order to test this relation, the capacitances of the empty cell and the cell with 0.001N NaCl which is the end product of titration was measured at different electrode distance. Results obtained have been shown in figure 2. The slopes



Fig, 2.

$\frac{dc_1}{dx}$ and $\frac{d(C_1+C_2)}{dx}$ have been obtained from the respective curves at a given value of x and the validity of the equation (2) was checked for each electrode distance.

It is interesting to note that the equation fits quite well above a separation of 3.5 cm. Since the equation contains C_1, the characteristic of the cell wall, C_2 that of the solution and their changes with electrode distance, it is clear that it throws sufficient light to the influence of the electrode distance which appears to depend upon the diameter (Chakravorty *et al*, 1964) of cell, the nature of the glass and that of the solution.

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